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METHOD OF TREATING WASTEWATER CONTAINIG AN ORGANIC SUBSTANCE
[YUKIBUTSU GANYU HAISUI NO SHORI HOHO]

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Specification

1. Title of the Invention

Method of Treating Wastewater Containing an Organic Substance

2. Claims

(1) A method of treating wastewater containing an organic substance by oxidation of the organic substance using ozone and hydrogen peroxide together, said method comprising the steps of:

adjusting pH of untreated wastewater to not higher than 4.5 by acid injection and aerating with air;

removing dissolved carbonate radicals;

subsequently adjusting pH to 6 to 8 by injection of an alkali agent; and

then performing hydrogen peroxide-added ozone treatment.

(2) The method of treating wastewater containing an organic substance according to Claim 1, wherein the aeration with air is done by sending and diffusing air into a degassing tower from a blower.

3. Detailed Description of the Invention

The present invention relates to a method of treating wastewater containing an organic substance with ozone and hydrogen peroxide.

Ozone is a strong oxidizer, which is generated by silent discharge using air or oxygen as a raw material. With development of large-size ozone generator, improvement in the performances, etc., ozone has been industrially used and practically used in various wastewater treatments. Ozone has been used in treating wastewater containing an organic substance, such as decolorizing of wastewater from dying plants, removal of phenol, cyan, etc., decolorizing of wastewater from treating human excrement, etc. In these treatments, a chemical property of ozone, which easily cleaves unsaturated bonds in various organic substances, is used. On the other hand, in these years, it has been more required to strengthen measures for environmental conservation and reuse wastewater, and thereby advanced treatment becomes necessary for more various wastewaters. In addition, development of effective COD removal technique based on Total COD (chemical oxygen demand) Regulations is especially demanded.

Under this circumstance, there is an attempt of COD removal by ozone, which is partially practically used. However, there are many COD components which hardly reacts

or does not react with ozone at all, and it is well known that there are many cases in which it is impossible to remove COD components only by ozone.

In order to eliminate such limitation in the use of ozone, a hydrogen peroxide-added ozone treatment method has been proposed.

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Fig. 1 is a system diagram of a conventional treatment method of this type. In this figure, [1] is an ozone generator; [2] is an ozone reaction tank; [3] is a diffuser to disperse ozone; [4] is a tank for an acid agent or an alkali agent for pH control; [6] is a untreated water tank; [7] is an acid or alkali agent injection pump; [8] is a hydrogen peroxide injection pump; [9] is a untreated water supply pump; and [10] is an exhaust ozone decomposer.

In the treatment method of Fig. 1, untreated water is supplied from the untreated water tank [6] to the ozone reaction tank [2] by the pump [9], and specified amounts of hydrogen peroxide and an acid or alkali agent are respectively injected in the untreated water supplied in the reaction tank [2] by the pumps [8] and [7]. The amount of the acid or alkali agent to inject is set to make the pH of the water to be treated in the reaction tank [2] in range of 6 to 8. Ozone-containing air or oxygen

(hereinafter referred to as "ozone-containing gas") generated in the ozone generator [1] becomes fine air bubbles by the diffuser [3], and moves up in the water to be treated. In the meantime, ozone in air bubbles is mostly consumed by the reaction, and a part of the ozone is exhausted. The exhausted ozone is removed at the exhaust ozone decomposer [10], and then discharged into air. The untreated water continuously supplied in the ozone reaction tank [2] is treated by reaction with the ozone, and taken out as treated water from the bottom of the reaction tank [2]. While a continuous treatment method is as described above, there is another method, a semi-batch treatment method, in which the reaction tank [2] is filled with untreated water and the untreated water is treated with ozone while injecting hydrogen peroxide and an acid or alkali agent in the reaction tank [2]. Even with the semi-batch treatment method, similar effects can be achieved.

Fig. 2 shows a plot of removed amount of TOC (total organic carbons) when sodium acetate aqueous solution, which is one of hardly oxidizable substances, is treated with ozone near neutral pH while changing the amount of hydrogen peroxide to add between 0 and 50 mg/L according to the treatment method of Fig. 1. Here, TOC before the treatment was 40 mg/L. From Fig. 2, it can be understood

that TOC can be removed if hydrogen peroxide is added, while TOC was hardly removed by ozone treatment without adding hydrogen peroxide. The amount of removed TOC increased with increase of the added amount of hydrogen peroxide. Accordingly, organic substances that could not be removed at all by conventional ozone treatments can be removed by ozone treatment using hydrogen peroxide together. An example of the treatment result by this method is shown in Table 1. Table 1 shows a result of treatment, in which constant amounts of hydrogen peroxide and ozone are added in various organic substance-containing aqueous solutions having TOC level of about 40 mg/L. In any of the organic substances, TOC was removed, and necessary amount ($\Delta O_3/\Delta TOC$, $\Delta O_3/\Delta TOD$) of ozone to remove a 1 weight unit of TOC and TOD (total oxygen demand) was about 10 and 3 weight units, respectively. Accordingly, it can be understood that the ozone use efficiency is high. Furthermore, the hydrogen oxide consumption is as small as about 1/10 of the ozone consumption.

Table 1 TOC Removal from Model Wastewater (under Constant Treatment Conditions)

Compound	TOC (mg/l)		$\Delta O_3/\Delta TOC$* (wt/wt)	$\Delta O_3/\Delta H_2O_2$** (wt/wt)	$\Delta O_3/\Delta TOD$ (wt/wt)
	Untreated water	Treated water			
methanol	37.5	2.3	12.9	15.2	3.3
ethanol	38.4	8.3	11.0	11.0	2.8
n-butanol	39.5	10.5	9.5	9.1	2.4
t-butanol	39.0	10.5	9.8	9.1	2.5
s-butanol	40.5	12.5	10.0	9.1	2.6
acetic acid (Na salt)	43.5	13.5	9.1	9.1	3.4
benzoic acid (Na salt)	44.2	11.1	11.1	12.3	3.9
propionic acid (Na salt)	43.0	7.5	6.9	8.3	2.2
acetone	41.0	13.0	9.1	8.3	2.6
methyl isobutyl ketone	45.3	20.7	9.9	8.3	3.0
phenol	42.5	9.5	9.6	10.5	3.1
ethanol amine	43.0	4.5	11.0	14.1	1.8
diethanol amine	42.3	7.4	11.6	13.5	2.5
ethylene glycol monomethyl ether	41.5	4.0	8.9	11.1	

*Necessary ozone amount ratio (by weight) for TOC removal.
**Consumption ratio of ozone and H_2O_2 (by weight)

As described above, the hydrogen peroxide-added ozone treatment method is a very effective method for removal of organic substances, but has the following drawbacks. If dissolved carbonate radicals such as carbonate ions or

bicarbonate ions are contained in untreated wastewater in a large amount, ozone and hydrogen peroxide are wastefully consumed. Accordingly, the above-described $\Delta O_3/\Delta TOC$ and $\Delta H_2O_2/\Delta TOC$ become larger and economic efficiency of the organic substance treatment is impaired. Fig. 3 shows plots to evaluate by $\Delta O_3/\Delta TOC$ and $\Delta H_2O_2/\Delta TOC$ the performance of removal of acetate ions when a sodium acetate aqueous solution, in which bicarbonate ions were added in the form of sodium bicarbonate, was treated by hydrogen peroxide-added ozone treatment under condition of pH 7.5. As described above, the result clearly shows impairment of the effect of removing organic substances by ozone and hydrogen peroxide. From this result, if 100 ppm (8.3×10^{-3} mol/L) bicarbonate radicals are contained as inorganic carbons in untreated water, 1.5 times the amount of ozone and 3 times the amount of hydrogen peroxide, which are required when bicarbonate radicals are not contained, to remove the same amount of TOC.

In order to eliminate the drawbacks of the above-described conventional hydrogen peroxide-added ozone treatment method, there is provided an invention, an object of which is to provide a method of treating wastewater containing an organic substance to efficiently remove organic substances by adjusting pH of untreated wastewater

to not higher than 4.5 by acid injection and aerating with air; removing dissolved carbonate radicals; and then performing hydrogen peroxide-added ozone treatment.

Fig. 4 is a system diagram showing a treatment method according to an embodiment of the invention. [11] is a degassing tower, [12] is a blower, [13] is a pump to send water to be treated by pressure, [14] is a pump for acid injection, and [15] is an acid storage tank.

Next, a treatment method shown in Fig. 4 will be fully described. The untreated water in the untreated water tank [6] is sent to the degassing tower [11] by the pump [9]. In the meantime, acid is injected from the acid storage tank [15] by the pump [14], and the pH is adjusted to not higher than 4.5. Under this condition, most of dissolved carbonate radicals exists in the form of carbonic acid. Since air is sent from the blower [11] and dispersed in the degassing tower [11], the dissolved carbonate level becomes lowered to a value, which is almost equilibrium with the carbon dioxide gas in air. The water to be treated, which was discharged from the degassing tower [11] is sent to the ozone reaction tank [2] by the pump [13], and the process after this is similar to the one shown in Fig. 1. The pH is re-adjusted to 6 to 8

by injection of an alkali agent, hydrogen peroxide is added, and ozone treatment is performed.

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In the above-described treatment method, the carbonate radicals dissolved in untreated water are removed by aeration with air under acidic condition having pH of not higher than 4.5, and the dissolved carbonate level becomes lowered to the level which is equilibrium with carbon dioxide level in air. Here, the dissolved carbon dioxide gas level at 20 °C is 5.1 mg/L since the solubility of carbon dioxide gas in water is 0.017 g/L and the carbon dioxide level in air is 0.03 %. In molarity, it is about 1.2×10^{-4} mol/L. Accordingly, the interference by remaining carbonate radicals can be reduced to negligible level as also obvious from Fig. 3. In other words, for treating untreated water containing 100 mg/L as inorganic carbons, treatment of organic substances can be conducted, in which the necessary amount of ozone can be reduced for 35 % and the necessary amount of hydrogen peroxide can be reduced for 65 %.

Here, in the above description, the method of aeration with air is not limited to the illustrated one, and may be also done with another means. In addition, the whole

treatment flow is not limited to the one shown in Fig. 4, and can be suitably changed.

As described above, according to the invention, since the method includes the steps of adjusting pH of untreated water to not higher than 4.5 by acid injection, aerating with air, removing carbonate radicals, and then performing hydrogen peroxide-added ozone treatment, interference by carbonate radicals can be eliminated and organic substances can be efficiently removed.

4. Brief Description of the Drawings

Fig. 1 is a system diagram showing a conventional hydrogen peroxide-added ozone treatment method; Fig. 2 shows a plot of a result of hydrogen peroxide-added ozone treatment; Fig. 3 shows relation between efficiency of hydrogen peroxide-added ozone treatment and concentration of coexistent bicarbonate ions; and Fig. 4 is a system diagram showing a treatment method according to an embodiment of the invention.

In the drawings, the same reference numerals indicate the same or equivalent portions. [1] is an ozone generator; [2] is an ozone reaction tank; [3] is a diffuser; [4] is an acid or alkali agent storage tank; [5] is a hydrogen peroxide storage tank; [6] is a untreated water tank; [7], [8], [9], [13], and [14] are pumps; [10]

is an exhaust ozone decomposer; [11] is a degassing tower; [12] is a blower; and [15] is an acid storage tank.

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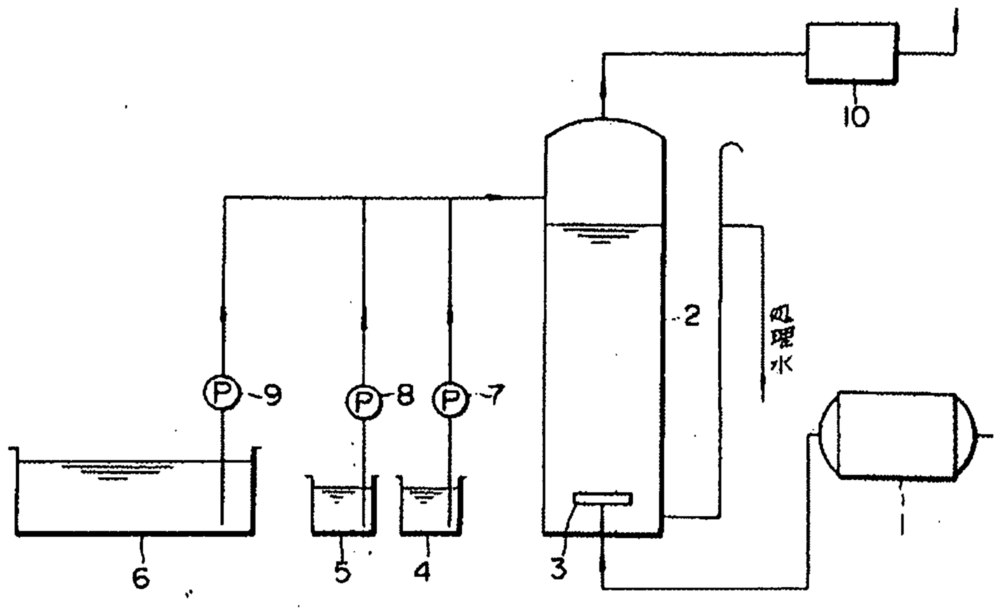
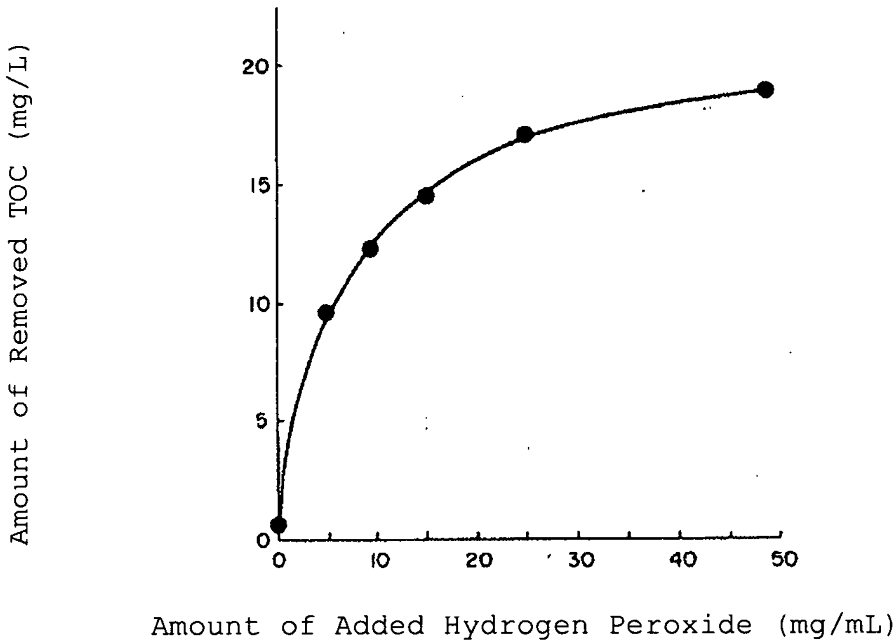


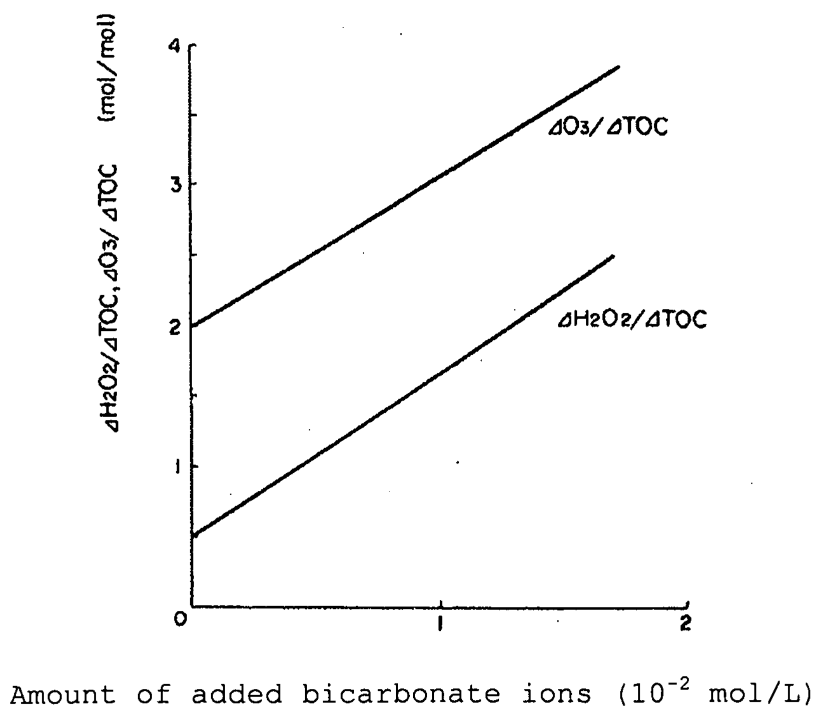
Treated water

[Fig. 1]



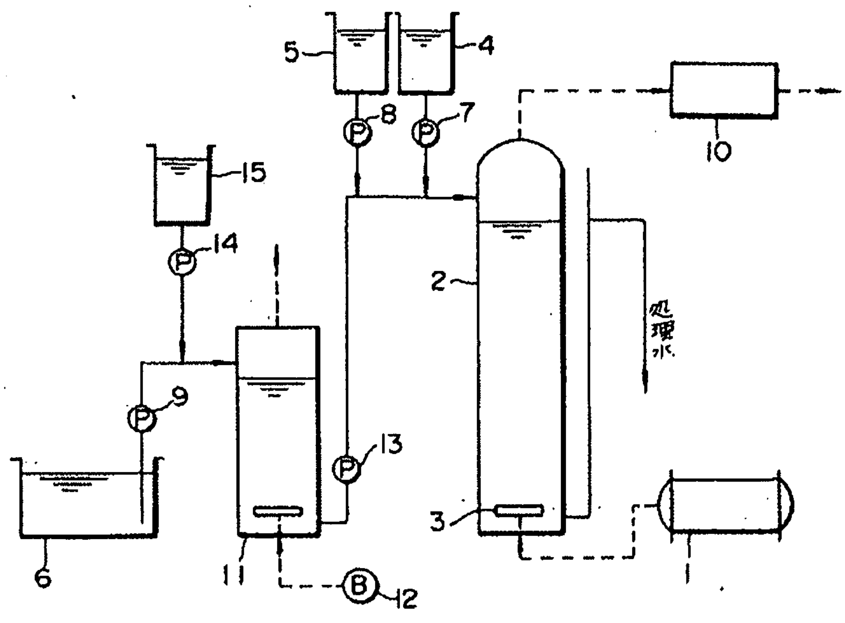
Amount of Removed TOC (mg/L)
20
15
10
5
0
0
10
20
30
40
50
Amount of Added Hydrogen Peroxide (mg/mL)

[Fig. 2]



ΔH2O2/ΔTOC, ΔO3/ΔTOC (mol/mol)
4
3
2
1
0
1
2
ΔO3/ΔTOC
ΔH2O2/ΔTOC
Amount of added bicarbonate ions (10^{-2} mol/L)

[Fig. 3]



Treated water

[Fig. 4]